A simple approach for charge renormalization of highly charged macro-ions

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We revisit the popular notion of effective or renormalized charge, which is a concept of central importance in the field of highly charged colloidal or polyelectrolyte solutions. Working at the level of a linear Debye-Hückel like theory only, we propose a simple, efficient and versatile method to predict the saturated amount of charge renormalization, which is however a non-linear effect arising at strong electrostatic coupling. The results are successfully tested against the numerical solutions of Poisson-Boltzmann theory for polyions of various shapes (planar, cylindrical and spherical), both in the infinite dilution limit or in confined geometry, with or without added electrolyte. Our approach, accurate for monovalent micro-ions in solvents like water, is finally confronted against experimental results, namely the crystallization of charged colloidal suspensions and the osmotic coefficient of B-DNA solutions.

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Our present understanding of charged macro-ions suspensions is essentially based on the DLVO theory, named after Derjaguin, Landau, Verwey and Overbeek [1]. This approach relies on a Poisson-Boltzmann (PB) mean-field description of the micro-ions clouds. An important prediction of the theory is the effective interaction pair potential between two macro-ions (e.g. colloids) in the solvent which, within a linearization approximation, takes the well-known Yukawa or Debye-Hückel (DH) form: $v(r) \sim Z^2 \exp(-\kappa r)/r$, where Z is the charge of the object and κ denotes the inverse Debye screening length. However, this approach becomes inadequate to describe highly charged objects for which the electrostatic energy of a micro-ion near the macro-ion surface largely exceeds k_BT, the thermal energy, and the linearization of PB equations is a priori not justified. In this case however, the electrostatic potential in exact [2] or mean-field [3–5] theories still takes a Debye-Hückel form far from the charged bodies, provided that the source of the potential is renormalized ($Z \to Z_{\text{eff}}$). The essential idea is that the micro-ions which suffer a high electrostatic coupling with the macro-ion accumulate in its immediate vicinity so that the decorated object (macro-ion *plus* captive counter-ions) may be considered as a single entity which carries an effective charge Z_{eff}, much lower (in absolute value) than the structural one. Within PB theory, Z and Z_{eff} coincide for low values of the structural charge, but Z_{eff} eventually reaches a saturation value Z_{sat} independent of Z when the bare charge increases [5,6].

Of course, the difficulty remains to predict Z_{sat} for a given suspension of macro-ions [4–7]. In the absence of any general analytical framework for the computation of the effective charge, this quantity is often considered as an adjustable parameter to fit experimental data [8,9]. In this Letter we show that a simple physical argument, at the level of the DH linearized description only, yields explicit (and in some favorable cases analytical) expressions for the effective charges at saturation, which compare well with both numerical solutions of non-linear PB theory and available experimental data.

For simplicity, we start by considering a unique highly (positively) charged sphere immersed in a symmetric 1:1 electrolyte of bulk ionic strength $I_0 = \kappa^2/(8\pi\ell_B)$, where $\ell_B = e^2/(4\pi\epsilon k_BT)$ is the Bjerrum length (ϵ being the dielectric constant of the solvent): $\ell_B = 7\,\text{Å}$ for water at room temperature. Within PB theory, the dimensionless electrostatic potential $\Phi = eV/k_BT$ obeys the relation

$$\nabla^2\Phi = \kappa^2 \sinh\Phi. \tag{1}$$

Far from macro-ion (where it is understood that Φ vanishes), the solution Φ_{PB} of Eq. (1) also obeys the linearized Poisson-Boltzmann (LPB) equation $\nabla^2\Phi = \kappa^2\Phi$, and therefore takes the Yukawa form $\Phi_{\text{LPB}} = Z_{\text{eff}}\ell_B \exp[\kappa(a-r)]/[r(1+\kappa a)]$, with a the radius of the sphere. Z_{eff} (in e units) is consequently defined here without ambiguity from the far field behaviour of Φ_{PB} (see [4,10,11] for alternative definitions of effective charges). Accordingly, a "non linear" region may be defined ($r \in [a, r^*]$), corresponding to Φ_{PB} larger than unity, where by definition of the cutoff r^*, $\Phi_{\text{LPB}}(r^*)$ is of order 1. In the limit of large κa, this "non-linear" region is however confined to the immediate vicinity of the macro-ion: $r^* \simeq a$. We consequently have the effective boundary condition $\Phi_{\text{LPB}}(a) \simeq \Phi_{\text{PB}}(r^*) = \mathcal{C}$, where $\mathcal{C}$ is a constant of order 1, which yields immediately $Z_{\text{eff}} = \mathcal{C}a(1+\kappa a)/\ell_B$. This argument assumes that the bare charge Z is high enough to have Φ_{PB} larger than unity close to the macro-ion, and therefore provides the saturation value of Z_{eff}, denoted hereafter as Z_{sat} [12]. We therefore easily obtain the non trivial dependence of this quantity upon physico-chemical parameters.

This picture of a decorated macro-ion –where the

"bound" counterions renormalizing the charge appear to have an electrostatic energy eV_0 balancing the thermal energy k_BT– may be rationalized as follows. In the limit of large κa, we perform an asymptotic matching of the non-linear PB planar solution (see [1]) to the linear solution $\Phi_{\rm LPB}$ in curved geometry. We obtain for high bare charges the same value of the contact potential $\Phi_{\rm LPB}(a) = 4$ (of order 1 as expected) so that $Z_{\rm sat} = 4a(1+\kappa a)/\ell_B$ [13]. Such a procedure provides by construction the correct large κa (low curvature) behaviour of $Z_{\rm sat}$, but we will show below that it remains fairly accurate down to κa of order 1.

Generalizing this approach, we consequently obtain the leading curvature saturated effective charge from the following analysis. For an isolated macro-ion of arbitrary shape in an electrolyte: *a)* find the electrostatic potential, $\Phi_{\rm LPB}$, solution of the *linearized* PB equations, supplemented by a *fixed potential boundary condition*: $\Phi_{\rm LPB}(\text{surface}) = \mathcal{C}$, where $\mathcal{C} = 4$ at leading order in curvature; *b)* deduce $Z_{\rm sat}$ from Gauss theorem at the surface of the object. In the case of an infinite cylinder (radius a, bare lineic charge λ), we obtain $\lambda_{\rm sat} = 2(\kappa a/\ell_B)K_1(\kappa a)/K_0(\kappa a)$, where K_0 and K_1 are the modified Bessel functions of orders 0 and 1.

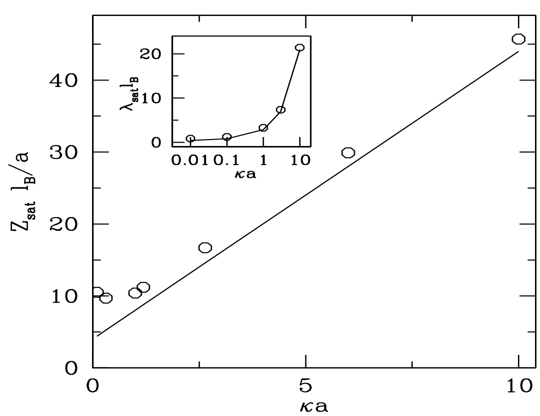

FIG. 1. Effective charge at saturation of an isolated spherical macro-ion (radius a) as a function of κa. The continuous line is the analytical expression given in the text, while the dots are the results extracted from the far field behaviour of the non-linear PB potential. In the inset, the same results for the cylinder geometry are shown on a log-linear scale.

In order to test the validity of our results, we have numerically solved the non-linear PB equation (1) for high Z values corresponding to the saturation regime, and computed the effective charge from the electrostatic potential at large distances (i.e. the value required to match $\Phi_{\rm LPB}$ to the far field $\Phi_{\rm PB}$ obtained numerically). Figure 1 compares the resulting PB effective charge to our expressions, for spherical and cylindrical macro-ions. The agreement becomes excellent at large κa as it should, and in the case of cylinders, even holds down to very small κa (0.01), a point which is not *a priori* expected. Finally, in the planar geometry our approach provides by construction the correct effective charge (compared to PB).

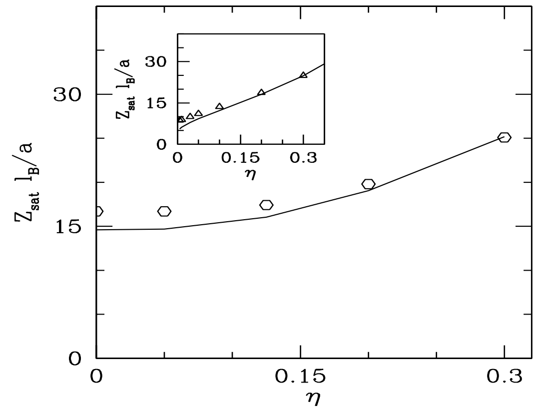

FIG. 2. Effective saturated charge of spherical macro-ions (radius a) as a function of volume fraction η for $\kappa a = 2.6$. The continuous line shows the effective charge computed using the prescription, while the dots are the results of the non-linear PB theory, following Ref. [5]. Inset: no-salt situation.

For spherical colloids, expressions reminiscent of that reported above can be found in the literature [4,14,15]. It seems however that the generality of the underlying method has been overlooked. In particular, our procedure may be extended to the finite concentration case, using the concept of Wigner Seitz (WS) cell [5]: the influence of the other macro-ions is accounted for by confining the macro-ion into a cell, with global electroneutrality. The size of the cell, R_{WS}, is computed from the density of macro-ions, while its geometry is chosen as to mimic the spatial structure of the macro-ions in the solution. Suppose that the system is in equilibrium with a reservoir of salt defined in terms of its Debye length κ^{-1}. We first linearize Eq. (1) around the value of potential at the cell boundary, $\Phi_R = \Phi(R_{WS})$, unknown at this point, which yields

$$\nabla^2 \delta\Phi = \kappa_\star^2\,(\gamma_0 + \delta\Phi) \tag{2}$$

where $\delta\Phi = \Phi - \Phi_R$, $\kappa_\star^2 = \kappa^2 \cosh(\Phi_R)$ and $\gamma_0 = \sqrt{1-(\kappa/\kappa_\star)^4}$. Note that the relevant screening length $\kappa_\star^{-1}$ (always smaller than κ^{-1}, a general feature for finite concentration) is not a parameter, and should be determined at the end of the calculation. Equation (2) is supplemented by two boundary conditions: the consistency constraint $[\delta\Phi(R_{WS}) = 0]$ and the global electroneutrality (which imposes a vanishing normal electric field at the WS boundary). To generalize the approach discussed in the limit of infinite dilution, we propose the following prescription (providing a third boundary condition): the *difference of potential* between the macro-ion and the WS surface is $\delta\Phi(a) = 4$. Here again, the effective charge is

obtained from Gauss theorem at the macro-ion's surface.

This generalized procedure is now explicited for a solution of spherical macro-ions with concentration ρ. The radius of the WS spherical cell is given as $R_{WS} = (4\pi\rho/3)^{-1/3}$. In this geometry, the (LPB) solution of Eq. (2) reads

$$\delta\Phi(r) = \gamma_0 \left[-1 + f_+ \frac{e^{\kappa_\star r}}{r} + f_- \frac{e^{-\kappa_\star r}}{r} \right] \qquad (3)$$

where $f_\pm = (\kappa_\star a \pm 1)/(2\kappa_\star)\exp(\mp\kappa_\star R_{WS})$. Our prescription allows to compute $\kappa_\star$, such that $\delta\Phi(a) = 4$. This equation is solved numerically for $\kappa_\star$ using a simple numerical Newton procedure. The effective charge follows from the gradient of $\delta\Phi(r)$ in Eq. (3) taken at $r = a$. The corresponding $Z_{\rm sat}$ as a function of volume fraction $\eta = 4\pi\rho a^3/3$ is displayed in Fig. 2, with a comparison to its counterpart deduced from the numerical solution of PB theory supplemented with the popular procedure proposed by Alexander et al [5]. On this figure, we have also plotted the results obtained without added salt [where the term sinhΦ on the r.h.s. of Eq. (1) is replaced by $\exp\Phi$, due to the absence of co-ions]. Our results are fully compatible with those obtained from Alexander's method, with a similar agreement for cylindrical macro-ions (not shown). It is eventually instructive to note that for a charged plane confined without added salt in a WS slab of width $2h$, Alexander's saturation surface charge may be computed analytically with the result [13] $\sigma_{\rm sat} = 2^{-3/2}\sinh(\pi/\sqrt{2})/(\ell_B h)$ whereas we obtain $\sigma_{\rm sat} = \sqrt{6}\text{Argcosh}(5)/(\pi\ell_B h)$ following our prescription. Both expressions agree within 10% and remarkably exhibit the same functional dependence on ℓ_B and density (through h).

That our prescription compares favorably with Alexander's procedure for the planar, cylindrical and spherical geometries, calls for the more stringent test of confronting our predictions against experimental data. We shall consider two specific situations corresponding to two different geometries: crystallization of charged colloidal suspensions and osmotic pressure in B-DNA solutions.

Crystallization of charged spheres. Investigation into the phase diagram of charged polystyrene colloids has been conducted experimentally by Monovoukas and Gast [8] and compared to the phase diagram of a system where particles interact through a Yukawa potential (deduced from extensive molecular dynamics simulations [16]). However this comparison requires an ad-hoc choice for $Z_{\rm eff}$. We use here the results we found for the effective charge as a function of ionic strength, which we insert into the numerical generic phase diagram of Yukawa systems [16]. We emphasize that there is *no adjustable parameter* in our equations since the radius of the polystyrene beads, the only parameter entering our description, was independently measured to be $a = 667$ Å. We only make the (reasonable) assumption that the bare charge Z of the colloids is large enough to have $Z_{\rm eff} \simeq Z_{\rm sat}$. The results for the melting line using our prescription for the effective charge are confronted to the experimental data in Fig. 3. We also plot the result for the melting line for an ad-hoc constant effective charge, $Z_{\rm eff} = 880$, as was proposed in [8] (while in our case the latter varies between 500 and 2000 on the melting curve). The observed agreement of our results illustrates both the pertinence of our prescription for $Z_{\rm sat}$ and the relevance of the PB saturation picture for macroions of large bare charge, for monovalent micro-ions in water.

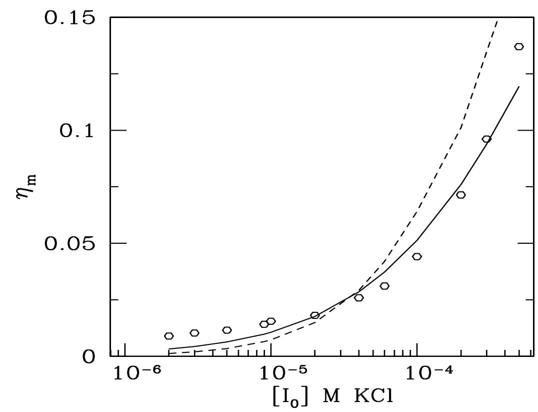

FIG. 3. Liquid-solid transition of charged polystyrene colloids: volume fraction for melting η_m as a function of salt ionic strength I_0. Dots are experimental points for the melting line extracted from Ref. [8]. The solid line is the theoretical prediction for the melting transition using our prescription for effective charges. The dashed line corresponds to $Z_{\rm eff} = 880$ (see text).

Osmotic coefficient of B-DNA. A similar test of our method may be performed for the cylindrical geometry using the experimental results for rigid cylindrical polyelectrolytes such as B-DNA [17]. We specifically consider the measurements of the osmotic coefficient $\phi = \Pi_{\rm osm}/\Pi_c$, defined as the ratio between the osmotic pressure $\Pi_{\rm osm}$ to the pressure Π_c of releasable counter-ions having bare density c_c ($\Pi_c = k_B T c_c$). Within the WS model, B-DNA macro-ions are confined into cylindrical cells, whose radius R_{WS} is related to the bare concentration of DNA counter-ions as $c_c = (\ell_{DNA}\pi R_{WS}^2)^{-1}$, with $\ell_{DNA} = 1.7$ Å the distance between charges along DNA. The osmotic pressure is related to the densities of micro-ions at the cell boundary: $\Pi_{\rm osm} = k_B T(\rho_+ + \rho_- - 2I_0)$ [18], which can be recast in the form $\Pi_{\rm osm} = k_B T(\kappa_\star^2 - \kappa^2)/(4\pi\ell_B)$ introducing the screening factor $\kappa_\star$ defined previously. This latter quantity is computed from our prescription, following the same lines as for the spherical case [see Eq. (3)].

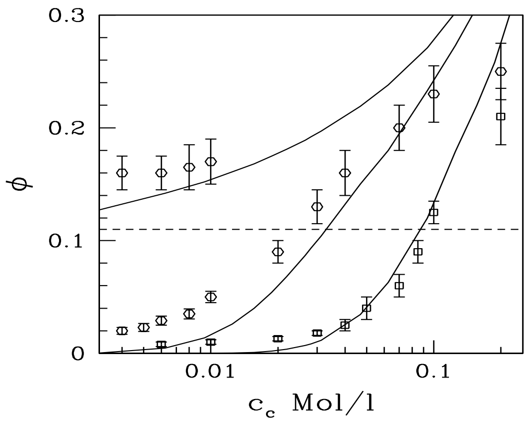

FIG. 4. Osmotic coefficient of B-DNA vs. density of DNA phosphate ions c_c, for $I_0 = 10$ mM, 2mM and 0 mM (from bottom to top). Dots: experiments of Refs. [17]; solid lines: present prescription; dashed line: prediction of Oosawa-Manning condensation theory.

In Fig. 4, the corresponding results for the osmotic coefficient are confronted against the experimental data of Refs. [17], showing again a good quantitative agreement. As in Ref. [18], we report the prediction of classical Oosawa-Manning condensation theory, for which the osmotic coefficient is constant [$\phi = \ell_{DNA}/(2\ell_B)$] at complete variance with the experiments. Again we emphasize that the only quantity introduced in our description is the diameter ($a = 10\,\text{Å}$) of DNA, known from independent measurements.

In conclusion, we have put forward a simple method of asymptotic matching to compute the effective charge at saturation for isolated macro-ions. In the situation of finite density, this method has been translated into a prescription, the validity of which has been assessed. This approach (mostly suited to describe the colloidal limit $\kappa a \gg 1$) amounts to consider the highly charged macro-ions as objects with constant electrostatic potential $\sim 4kT/e$, independently of shape and physicochemical parameters (size, added 1:1 electrolyte…). As a general result we find that the effective charge is an *increasing* function of κ, which stems from the reduction of the attraction between the counter-ions and the macro-ion. Addition of salt consequently brings two antagonist effects on the effective Coulombic interaction between macro-ions: the range of the interaction decreases due to screening, while the amplitude increases due to the effective charge. The competition between these two effects might be a key point in the understanding of these systems.

An important question concerning our approach, is that of the validity of PB theory for highly charged macro-ions. Within PB, micro-ions correlations are neglected, but the approach may still allow to describe high macro/micro-ions couplings: in particular, for monovalent micro-ions in water at room temperature, micro-ions correlations are negligible for all known macro-ions. This may no longer be the case in presence of multi-valent micro-ions. More generally, PB is a reasonable approximation when the macro-ion size a is much larger than ℓ_B [19], and the saturation plateau of Z_{eff} as a function of the bare charge Z is an important physical phenomenon that our approach allows to capture. When a becomes of the same order as ℓ_B the amount of counter-ion "condensation" found in molecular dynamics or Monte Carlo simulations is larger than predicted by PB [19,20]; our method for Z_{sat} therefore provides an upper bound for the effective charge. It is moreover noteworthy that for B-DNA where $a/\ell_B \simeq 1.4$, our approach still gives a valuable first approximation, and that omission of charge renormalization leads to spurious results (such as negative osmotic coefficients corresponding to an unphysical phase transition at physiological salt concentrations).

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